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**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY DOCKET NUMBER <b>IN-5531</b>	U.S. APPLICATION NUMBER (SEE 37 CFR 1.51) <b>10/009394</b>	
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/03267</b>	INTERNATIONAL FILING DATE <b>12. April 2000 (12.04.00)</b>	PRIORITY DATE CLAIMED <b>06. May 1999 (06.05.99)</b>
TITLE OF INVENTION: <b>HIGHLY SCRATCH-RESISTANT MULTICOAT SYSTEM ITS PREPARATION AND USE</b>		

APPLICATION(S) FOR DO/EO/US: **Maxime Euring ALLARD, Cyrille JAECQUES, Isabelle KAUFFER**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ have been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(C)(2)).
7. ☒ Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annex to the International Preliminary Examination Report under PCT Article 36

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A Change of power of attorney and/or address letter.
16. ☒ Other items or information:

**A copy of the cover sheet from the PCT Published Application  
A copy of the cover sheet from the Priority Document**

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*Marjorie Ellis*  
Marjorie Ellis



PATENT  
(Practitioner's Docket No. IN-5531)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Maxime Euring ALLARD  
Cyrille JAECQUES  
Isabelle KAUFFER

Serial No.: This application is a National  
Phase of Patent Application  
PCT/EP00/03267 filed 12. April 2000.

Filed: October 25, 2001

For: HIGHLY SCRATCH-RESISITANT  
MULTICOAT SYSTEM ITS  
PREPARATION AND USE

Group Art Unit: Not Assigned

Examiner: Not Assigned

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Marjorie Ellis

**PRELIMINARY AMENDMENT UNDER 37 CFR § 1.115**

Commissioner for Patents

Washington, D.C. 20231

Dear Sir:

This preliminary amendment is submitted with the application for entry into  
the U.S. National Phase under Chapter II. This application is based on PCT/EP00/0  
filed on 2000.

In connection with the filing of this National Phase application, please make  
the following preliminary amendments.

Claims pending after entry of the Preliminary amendment are 1-14.

## CLEAN COPY OF THE AMENDMENTS

### IN THE SPECIFICATION

After the title, please insert --This application is a National Phase Application of Patent Application **PCT/EP00/03267** filed on 12 April 2000--

### IN THE CLAIMS:

Please substitute claims 1-14 as follows.

1. (Amended) A highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, produced by
  - (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, and partially curing it,
  - (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and optionally thermally, to the surface of the clearcoat film I, and
  - (3) curing the clearcoat films I and II conjointly with actinic radiation and thermally.
2. (Amended) A highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, produced by
  - (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, curing it and roughening it,
  - (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and optionally, thermally, to the outer surface of the clearcoat film I, and
  - (3) curing the clearcoat film II with actinic radiation and, optionally, thermally.

3. (Amended) A highly scratch-resistant, multicoat color and/or effect coating system B for a primed or unprimed substrate, produced by
- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and, optionally, with actinic radiation, to the surface of the substrate and drying it without curing,
  - (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them,
  - (3) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and, optionally, thermally, to the surface of the clearcoat film I, and
  - (4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.
4. (Amended) A highly scratch-resistant multicoat color and/or effect coating system B for a primed or unprimed substrate, made by
- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and, optionally, with actinic radiation to the surface of the substrate and drying it without curing,
  - (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,
  - (3) curing the basecoat film III and clearcoat film(s) I conjointly, thermally and with actinic radiation,
  - (4) roughening the outer surface of the clearcoat film(s) I,

- (5) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and, optionally thermally, to the outer surface of the clearcoat film I, and
- (6) curing the clearcoat film II with actinic radiation and, optionally, thermally.

5. (Amended) A process for producing a highly scratch-resistant multicoat clearcoat system (A) on a primed or unprimed substrate, comprising

- (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of a substrate, and partially curing it, and
- (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and, optionally thermally, to the surface of the clearcoat film I, and then
- (3) curing the clearcoat films I and II conjointly with actinic radiation and thermally.

6. (Amended) A process for producing a highly scratch-resistant multicoat clearcoat system A on a primed or unprimed substrate, comprising

- (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of a substrate, curing it and roughening it,
- (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and, optionally thermally, to the outer surface of the clearcoat film(s) I, and
- (3) curing the clearcoat film II with actinic radiation and, optionally thermally.

7. (Amended) A process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, comprising
- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and, optionally, with actinic radiation to the surface of the substrate and drying it without curing,
  - (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them,
  - (3) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and, optionally, thermally, to the surface of the clearcoat film I, and
  - (4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.
8. (Amended) A process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, comprising
- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and, optionally, with actinic radiation to the surface of the substrate and drying it without curing,
  - (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,
  - (3) curing the basecoat film III and clearcoat film I conjointly, thermally and with actinic radiation,
  - (4) roughening the outer surface of the clearcoat film I,

- (5) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and, optionally, thermally, to the outer surface of the clearcoat film I, and
- (6) curing the clearcoat film II with actinic radiation and, optionally, thermally.

9. (Amended) The clearcoat system A of claim 1, wherein the coating material II comprises nanoparticles based on silicon dioxide, aluminum oxide and zirconium oxide.

10. (Amended) The clearcoat system A of claim 1 wherein the coating material I comprises

- (a1) at least one constituent comprising
  - (a11) at least two functional groups which serve for crosslinking with actinic radiation, and optionally
  - (a12) at least one functional group which is able to undergo thermal crosslinking reactions with a complementary functional group (a22) in the constituent (a2), and
- (a2) at least one constituent comprising
  - (a21) at least two functional groups which serve for crosslinking with actinic radiation, and
  - (a22) at least one functional group which is able to undergo thermal crosslinking reactions with a complementary functional group (a12) in the constituent (a1), and optionally,

one or more members selected from the group consisting of

- (a3) at least one photoinitiator,
- (a4) at least one thermal crosslinking initiator,
- (a5) at least one reactive diluent curable thermally and/or with actinic radiation,



(a6) at least one coatings additive,  
(a7) at least one thermally curable constituent,  
and mixtures thereof, with the proviso that the coating material I comprises at  
least one thermally curable constituent (a7) if the constituent (a1) contains no  
functional group (a12).

11. (Amended) The clearcoat system A of claim 10, wherein the functional groups (a11) and (a21) comprise olefinically unsaturated groups or epoxide groups,.
12. (Amended) The clearcoat system A, wherein the constituent (a1) comprises a urethane (meth)-acrylate and the constituent (a2) comprises a member selected from the group consisting of (meth)acrylate-functional (meth)acrylate copolymer containing free isocyanate groups, (meth)acrylate-functional polyisocyanate, and mixtures thereof.
13. (Amended) The process of claim 5, wherein the substrate is selected from the group consisting of automotive OEM substrates, automotive refinish substrates, plastics substrates, furniture substrates, coil substrates and container substrates.
14. (Amended) An article selected from the group consisting of motor vehicles, plastic parts, furniture items, industrial parts, coil, and containers, produced by the process of claim 5.

### **REMARKS**

Upon entry of the present amendment claims 1-14 are pending in the application. Claims 1-14 have been amended in accordance with the requirements of U.S. patent practice. Applicants respectfully request entry of the preliminary amendment.

## MARKED UP COPY OF THE AMENDMENTS

### IN THE SPECIFICATION

After the title, please insert --This application is a National Phase Application of Patent Application **PCT/EP00/03267** filed on 12 April 2000--

### IN THE CLAIMS:

Please substitute claims 1-14 as follows.

1. (Amended) A highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, [producible]produced by
  - (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, and partially curing it, [and]
  - (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and [also, if desired, optionally thermally, [comprising nanoparticles, ]to the surface of the clearcoat film[(s)] I, and [then]
  - (3) curing the clearcoat films I and II conjointly with actinic radiation and thermally.
2. (Amended) A highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, [producible]produced by
  - (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, curing it and roughening it,

- (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and [also, if desired,] optionally, thermally, [comprising nanoparticles, ] to the outer surface of the clearcoat film[(s)] I, and [then]
- (3) curing the clearcoat film II with actinic radiation and, [if desired] optionally, thermally.

3. (Amended) A highly scratch-resistant, multicoat color and/or effect coating system B for a primed or unprimed substrate, [producible] produced by

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and[ also], [if desired] optionally, with actinic radiation, to the surface of the substrate and drying it without curing,
- (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them, [and]
- (3) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and[ also], [if desired] optionally, thermally, [comprising nanoparticles, ] to the surface of the clearcoat film[(s)] I, and [then]
- (4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

4. (Amended) A highly scratch-resistant multicoat color and/or effect coating system B for a primed or unprimed substrate, [producible] made by

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and[ also], [if desired] optionally, with actinic radiation to the surface of the substrate and drying it without curing,

- (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,
- (3) curing the basecoat film III and clearcoat film(s) I conjointly, thermally and with actinic radiation,
- (4) roughening the outer surface of the clearcoat film(s) I,
- (5) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and[ also], [if desired]optionally, thermally, [comprising nanoparticles,] to the outer surface of the clearcoat film[(s)] I, and [then]
- (6) curing the clearcoat film II with actinic radiation and, [if desired]optionally, thermally.

5. (Amended) A process for producing a highly scratch-resistant multicoat clearcoat system (A) on a primed or unprimed substrate, [which comprises]comprising

- (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of [the]a substrate, and partially curing it, and
- (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and[ also], [if desired,]optionally thermally, [comprising nanoparticles,] to the surface of the clearcoat film[(s)] I, and then
- (3) curing the clearcoat films I and II conjointly with actinic radiation and thermally.

6. (Amended) A process for producing a highly scratch-resistant multicoat clearcoat system A on a primed or unprimed substrate, [which comprises]comprising

- (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of [the]a substrate, curing it and roughening it,
- (2) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and[ also], [if desired,]optionally thermally, [comprising nanoparticles,] to the outer surface of the clearcoat film(s) I, and [then]
- (3) curing the clearcoat film II with actinic radiation and, [if desired,]optionally thermally.

7. (Amended) A process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, [which comprises]comprising

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and[ also], [if desired]optionally, with actinic radiation to the surface of the substrate and drying it without curing,
- (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them, [and]
- (3) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and[ also], [if desired]optionally, thermally, [comprising nanoparticles, ]to the surface of the clearcoat film[(s)] I, and [then]
- (4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

8. (Amended) A process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, [which comprises]comprising

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and[ also], [if desired]optionally, with actinic radiation to the surface of the substrate and drying it without curing,
- (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,
- (3) curing the basecoat film III and clearcoat film[(s)] I conjointly, thermally and with actinic radiation,
- (4) roughening the outer surface of the clearcoat film[(s)] I,
- (5) applying a further clearcoat film II of a coating material II comprising nanoparticles and curable with actinic radiation and[ also], [if desired]optionally, thermally, [comprising nanoparticles, ]to the outer surface of the clearcoat film[(s)] I, and [then]
- (6) curing the clearcoat film II with actinic radiation and, [if desired]optionally, thermally.

9. (Amended) The clearcoat system A [as claimed in]of claim 1[ or 2],[ the multicoat system B as claimed in claim 3 or 4, the process for producing the clearcoat system A as claimed in claim 5 or 6, or the process for producing the multicoat system B as claimed in claim 7 or 8,] wherein the coating material II comprises nanoparticles based on silicon dioxide, aluminum oxide and zirconium oxide.
10. (Amended) The clearcoat system A [as claimed in any ]of claim[s] 1[, 2 and 9, the multicoat system B as claimed in any of claims 3, 4 and 9, the process

for producing the clearcoat system A as claimed in any of claims 5, 6 and 9, or the process for producing the multicoat system B as claimed in any of claims 7 to 9,] wherein the coating material I comprises

- (a1) at least one constituent [containing]comprising
  - (a11) at least two functional groups which serve for crosslinking with actinic radiation, and [if desired] optionally
  - (a12) at least one functional group which is able to undergo thermal crosslinking reactions with a complementary functional group (a22) in the constituent (a2), and
- (a2) at least one constituent [containing]comprising
  - (a21) at least two functional groups which serve for crosslinking with actinic radiation, and
  - (a22) at least one functional group which is able to undergo thermal crosslinking reactions with a complementary functional group (a12) in the constituent (a1), and [also, if desired]optionally,

one or more members selected from the group consisting of

- (a3) at least one photoinitiator,
- (a4) at least one thermal crosslinking initiator,
- (a5) at least one reactive diluent curable thermally and/or with actinic radiation,
- (a6) at least one coatings additive, [and/or]
- (a7) at least one thermally curable constituent,

and mixtures thereof, with the proviso that the coating material I comprises at least one thermally curable constituent (a7) if the constituent (a1) contains no functional group (a12).

11. (Amended) The clearcoat system A[, the multicoat system B, the process for producing the clearcoat system A or the process for producing a multicoat system B as claimed in] of claim 10, wherein the functional groups (a11) and

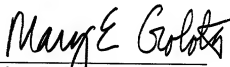


(a21) comprise olefinically unsaturated groups or epoxide groups, [especially olefinically unsaturated groups, hydroxyl groups in the case of the functional groups (a12) and [lacuna] in the case of the complementary functional groups (a22) and isocyanate groups].

12. (Amended) The clearcoat system A[, the multicoat system B, the process for producing the clearcoat system A or the process for producing a multicoat system B as claimed in]of claim 10[ or 11], wherein the constituent (a1) comprises a urethane (meth)-acrylate and the constituent (a2) comprises a member selected from the group consisting of(meth)acrylate-functional (meth)acrylate copolymer containing free isocyanate groups, [and/or comprises a ](meth)acrylate-functional polyisocyanate, and mixtures thereof.
  
13. (Amended) The [use of the clearcoat system A as claimed in any of claims 1, 2 and 9 to 12, of the multicoat systems B as claimed in any of claims 3, 4 and 9 to 12, of the ]process [for producing the clearcoat system A as claimed in any ]of claim[s] 5, [6 and 9 to 12, or of the process for producing the multicoat system B as claimed in any of claims 7 to 12, in]wherein the substrate is selected from the group consisting of automotive OEM [finishing]substrates, automotive refinish substrates, [the coating of ]plastics substrates, furniture [coating]substrates, [and industrial coating, including] coil [coating]substrates and container [coating]substrates.
  
14. (Amended) An article selected from the group consisting of motor vehicles, plastic parts, furniture items, [or other part for private or ]industrial [use]parts, [including a ]coil, [or ]and containers, [comprising at least one clearcoat system A as claimed in any of claims 1, 2 and 9 to 12, at least one multicoat system B as claimed in any of claims 3, 4 and 9 to 12, at least one clearcoat system A ]produced [with the aid of]by the process [as claimed in any ]of claim[s] 5[, 6 and 9 to 12, and/or at least

one multicoat system B produced with the aid of the process as claimed in any of claims 7 to 12].

Respectfully Submitted,



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PAT 99164 PCT  
BASF Coatings AG

April 3, 2000

**Highly scratch-resistant multicoat system, its  
preparation and use**

The present invention relates to a novel, highly  
5 scratch-resistant multicoat clearcoat system based on  
at least two coating materials curable with actinic  
radiation. The present invention further relates to the  
use of the novel, highly scratch-resistant multicoat  
clearcoat in automotive OEM finishing and refinish,  
10 industrial coating, including coil coating and  
container coating, the coating of plastics, and  
furniture coating. The present invention further  
relates to a novel process for producing multicoat  
clearcoat systems.

15 Automobile bodies, plastic parts for automobiles or  
domestic appliances, and industrial components are  
nowadays protected by a clearcoat. The clearcoat may be  
used as the sole coat or else may form the topmost coat  
20 of a multicoat topcoat system.

Automobile bodies in particular are provided  
extensively with a multicoat topcoat system. Clearcoats  
are frequently applied as the final coat. Materials  
25 suitable for this purpose are the customary and known  
one-component (1K), two-component (2K), multicomponent  
(3K, 4K) powder clearcoat or powder slurry clearcoat  
materials, or UV-curable clearcoat materials.

One-component (1K), two-component (2K) or multicomponent (3K, 4K) clearcoat materials are described, for example, in the patents US-A-5 474 811, US-A-5 356 669, US-A-5 605 965, WO 94/10 211, 5 WO 94/10 212, WO 94/10 213, EP-A-0 594 068, EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992, WO 94/22 969, EP-A-0 596 460 and WO 92/22 615.

10 Powder clearcoat materials are known, for example, from the German patent DE-A-42 22 194 or from the BASF Lacke + Farben AG product information bulletin "Pulverlacke" [powder coating materials], 1990.

15 A powder coating material which is curable thermally and with actinic radiation is known from the European patent EP-A-0 844 286. It comprises an unsaturated binder and a second resin, copolymerizable with the first, and also a photoinitiator and a thermal initiator, and is accordingly curable thermally and 20 with actinic radiation. However, this dual-cure powder coating material is used as a pigmented topcoat material, which is cured superficially with UV light and thermally in the regions close to the substrate. The patent does not reveal whether this known powder 25 coating material is also suitable for producing clearcoats, especially in multicoat systems.

Powder slurry coating materials comprise powder coating materials in the form of aqueous dispersions. Slurries

of this kind are described, for example, in the U.S. patent US-A-4 268 542 and in the German patent applications DE-A-195 18 392.4 and DE-A-196 13 547 and in the German patent application DE-A-198 14 471.7, which was unpublished at the priority date of the present specification.

UV-curable clearcoat materials are disclosed, for example, by the patents EP-A-0 540 884, EP-A-0 568 967, and US-A-4 675 234.

Each of these clearcoat materials has specific strengths and weaknesses. Using these clearcoat materials, multicoat systems which satisfy the optical requirements are obtained. However, the scratch-resistant one-component (1K) clearcoat materials are sometimes not sufficiently weathering-resistant, whereas the weathering-resistant two-component (2K) or multicomponent (3K, 4K) clearcoat materials are often not sufficiently scratch-resistant. Certain one-component (1K) clearcoat materials are indeed scratch-resistant and weathering-stable but, in combination with frequently employed waterborne basecoat materials, exhibit surface defects such as shrinkage (wrinkling).

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Powder clearcoat materials, powder slurry clearcoat materials and UV-curable clearcoat materials, on the other hand, exhibit a not entirely satisfactory

intercoat adhesion, without completely solving the problems of scratch resistance or etch resistance.

EP-A-0 568 967 discloses a process for producing  
5 multicoat systems in which a thermally curable  
clearcoat film is applied by the wet-on-wet technique  
to a pigmented basecoat film, after which the two films  
are heat-cured together. Atop the cured clearcoat there  
is subsequently applied at least one further clearcoat  
10 film based on coating materials curable with actinic  
radiation, and curing is carried out with actinic  
radiation, or thermally and with actinic radiation.  
This process gives clearcoats of high chemical  
resistance and optical quality. However, the scratch  
15 resistance is not satisfactory.

Furthermore, EP-A-0 568 967 discloses a process in  
which a coating material curable with actinic radiation  
is applied to the pigmented basecoat film and cured.  
20 Subsequently, a further coat of the same coating  
material is applied and is cured with actinic  
radiation. Although this results in a highly glossy  
surface without perceptible texture, the clearcoat in  
question yellows. Additionally, the scratch resistance  
25 still leaves something to be desired.

Recently, materials known as sol-gel clearcoats and  
based on siloxane-containing coating formulations have  
been developed which are obtained by hydrolysis and  
condensation of silane compounds. These coating

materials, which are used as coating compositions on plastics, are described, for example, in the German patents DE-A-43 03 570, 34 07 087, 40 11 045, 40 25 215, 38 28 098, 40 20 316, and 41 22 743.

5

Sol-gel clearcoats impart very good scratch resistance to substrates made of plastic, such as spectacle lenses or motorcycle helmet visors, for example. This scratch resistance is not achieved by the known OEM (original equipment manufacturing) clearcoat materials normally used for the original finishing of vehicles. The automobile industry is now demanding that this improved scratch resistance be transferred to the clearcoats used in the finishing of automobiles as well. The aim here in particular is to provide better protection to those parts of the automobile bodies which are subject to particularly severe stresses, such as hoods, fenders, sills or doors in the door-handle region.

20 Replacing the OEM clearcoat materials or OEM powder slurry clearcoat materials commonly used in automotive finishing by sol-gel clearcoat materials, however, is not immediately possible, since the clearcoats are too brittle for this purpose, for example, or because the  
25 optical properties (appearance) achieved during the attempt to adapt them to the OEM requirements are in many cases poor. Furthermore, they cannot be applied at thicknesses above 8 to 10  $\mu\text{m}$ . Moreover, constituents of the sol-gel clearcoat materials may "strike through"

during their drying and/or curing: that is, they are absorbed by the substrate, and, as a result, the clearcoats in question lose hardness. Above all, however, the sol-gel clearcoat materials are too  
5 expensive.

The economically more favorable use of the sol-gel clearcoat materials as an additional coat over the clearcoats used to date gives rise to adhesion problems  
10 within the multicoat clearcoat system, between the clearcoat and the sol-gel coat, these problems arising in particular after stone chipping and on exposure to condensation. In some cases this problem is exacerbated by the adhesion between the clearcoat and the substrate  
15 also being affected.

These problems may be solved to a certain extent by subjecting the clearcoat film that is to be coated with the sol-gel clearcoat material to only partial curing,  
20 so that on conjoint curing the sol-gel coating may be anchored chemically, so to speak, on the clearcoat film. However, the second clearcoat film requires a long oven drying time to cure, which is a considerable disadvantage.

25

It is an object of the present invention to provide a novel multicoat clearcoat system which no longer has the disadvantages of the prior art but which instead is easy to produce, highly scratch-resistant, stable to



weathering, free from yellowing, hard, flexible, and free from surface defects, exhibits a high level of adhesion to all substrates and within the clearcoat system too, and may be produced in the high coat thickness needed for an outstanding overall appearance. A further object of the present invention is to provide a new process for producing such single-coat or multicoat clearcoats from at least two coating materials curable with actinic radiation.

10

Accordingly we have found the novel, highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, said system being producible by

15

(1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, and partially curing it, and

20

(2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

25

(3) curing the clearcoat films I and II conjointly with actinic radiation and thermally.

As an alternative to this, we have found the further novel, highly scratch-resistant multicoat clearcoat system A for a primed or unprimed substrate, said system being producible by

5

- (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, curing it and roughening it,

10

- (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

15

- (3) curing the clearcoat film II with actinic radiation and, if desired, thermally.

20 The two novel, highly scratch-resistant multicoat clearcoat systems A are referred to below as the "clearcoat systems A of the invention".

We have also found the novel process for producing a  
25 highly scratch-resistant multicoat clearcoat system A on a primed or unprimed substrate, which involves

- (1) applying at least one clearcoat film I of a coating material I curable thermally and with

actinic radiation to the surface of the substrate,  
and partially curing it, and

5 (2) applying a further clearcoat film II of a coating  
material II curable with actinic radiation and  
also, if desired, thermally, comprising nano-  
particles, to the surface of the clearcoat film(s)  
I, and then

10 (3) curing the clearcoat film I and II conjointly with  
actinic radiation and thermally.

As an alternative to this, we have found the further  
novel process for producing a highly scratch-resistant  
15 multicoat clearcoat system A on a primed or unprimed  
substrate, which involves

(1) applying at least one clearcoat film I of a  
coating material I curable thermally and with  
20 actinic radiation to the surface of the substrate,  
curing it and roughening it,

(2) applying a further clearcoat film II of a coating  
material II curable with actinic radiation and  
25 also, if desired, thermally, comprising nano-  
particles, to the outer surface of the clearcoat  
film(s) I, and then

- (3) curing the clearcoat film II with actinic radiation and, if desired, thermally.

The two new processes for producing highly scratch-resistant clearcoat systems A are referred to below as "processes A of the invention".

We have additionally found the novel, highly scratch-resistant multicoat color and/or effect coating system  
10 B for a primed or unprimed substrate, which is producible by

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III  
15 curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,
- (2) applying at least one clearcoat film I of a  
20 coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them, and
- (3) applying a further clearcoat film II of a coating  
25 material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

(4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

5 As an alternative to this, we have also found the novel, highly scratch-resistant multicoat color and/or effect coating system B for a primed or unprimed substrate, which is producible by

10 (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,

15 (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,

20 (3) curing the basecoat film III and clearcoat film(s) I conjointly, thermally and with actinic radiation,

25 (4) roughening the outer surface of the clearcoat film(s) I,

(5) applying a further clearcoat film II of a coating material II curable with actinic radiation and

also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

- 5 (6) curing the clearcoat film II with actinic radiation and, if desired, thermally.

In the text below, the novel multicoat color and/or effect coating systems B are referred to as the  
10 "multicoat systems B of the invention".

Furthermore, we have found the novel process for producing a highly scratch-resistant multicoat color and/or effect coating system B of a primed or unprimed  
15 substrate, which involves

- (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with  
20 actinic radiation to the surface of the substrate and drying it without curing,
- (2) applying at least one clearcoat film I of a coating material I curable thermally and with  
25 actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them, and
- (3) applying a further clearcoat film II of a coating material II curable with actinic radiation and

also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

- 5 (4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

10 As an alternative to this, we have found the further novel process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, which involves

- 15 (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,
- 20 (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,
- 25 (3) curing the basecoat film III and clearcoat film(s) I conjointly, thermally and with actinic radiation,

(4) roughening the outer surface of the clearcoat film(s) I,

5 (5) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

10 (6) curing the clearcoat film II with actinic radiation and also, if desired, thermally.

In the text below, the two new processes are referred to as the "processes B of the invention".

15

In the context of the present invention, the term "thermal curing" denotes the heat-initiated curing of a film of a coating material, usually using a separate crosslinking agent. This is commonly referred to by  
20 those in the art as external crosslinking. Where the crosslinking agents have already been built into the binders, the term self-crosslinking is used. In accordance with the invention, external crosslinking is of advantage and is therefore employed with preference.

25

In the context of the present invention, actinic radiation means electron beams or, preferably, UV radiation. Curing by UV radiation is normally initiated by free-radical or cationic photoinitiators and in



terms of its mechanism is a free-radical or cationic photopolymerization.

Where thermal curing and curing with actinic light are  
5 employed conjointly for one coating material, the term "dual cure" is also used.

In the light of the prior art it was surprising and unforeseeable for the skilled worker that the very  
10 complex problem on which the present invention is based might be solved with the aid of the clearcoat system A of the invention and of the multicoat system B of the invention and also of the processes of the invention for producing them. A particular surprise is that not  
15 only the intercoat adhesion within the clearcoat system A of the invention but also the adhesion to the basecoat III within the multicoat system B of the invention are improved to an extent far beyond that known. The clearcoat system A of the invention and the  
20 multicoat system B of the invention have excellent optical properties, in particular a high level of fullness, high DOI values, high gloss, and no yellowing. As a consequence of the dual curing, even complex components and shaped parts may be fully cured  
25 in their shadow regions in a simple manner. With all these advantages, the clearcoat system A of the invention and the multicoat system B of the invention are also of outstanding weathering and chemical stability. Not least, however, they are extremely

scratch-resistant and withstand even treatment with steel wool. In particular, however, they are not damaged by the equipment commonly employed in carwash installations.

5

The clearcoat system A of the invention is outstandingly suitable for the coating of a primed or unprimed substrate.

- 10 Suitable coating substrates are all surfaces which are amenable to combined curing using heat and actinic radiation, examples being metals, plastics, wood, ceramic, stone, textile, fiber composites, leather, glass, glass fibers, glass wool, rockwool, mineral- and
- 15 resin-bound building materials, such as plasterboard, cement slabs or rooftiles. Accordingly, the clearcoat system A of the invention is also suitable for applications outside of automotive finishing, in particular for the coating of furniture and for
- 20 industrial coating, including coil coating and container coating. In the context of industrial coatings, it is suitable for coating virtually all parts for private or industrial use, such as radiators, domestic appliances, small metal parts, hub caps or
- 25 wheel rims. The clearcoat system A of the invention is particularly suitable as a coating for basecoats, preferably in the automobile industry. It is particularly suitable as a clearcoat over waterborne basecoats based on polyesters, polyurethane resins and

amino resins, especially as part of the multicoat system B of the invention.

With the clearcoat system A of the invention or with  
5 the multicoat system B of the invention it is also possible, in particular, to coat primed or unprimed plastics such as, for example, ABS, AMMA, ASA, CA, CAB, EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE, LLDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF,  
10 SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM and UP (abbreviations to DIN 7728T1). The plastics to be coated may of course also comprise polymer blends, modified plastics, or fiber-reinforced plastics. The system may also be used to coat plastics commonly used  
15 in vehicle construction, especially motor vehicle construction.

Nonfunctionalized and/or nonpolar substrate surfaces may be subjected prior to coating in a known manner to  
20 a pretreatment, such as with a plasma or by flaming.

The clearcoat system A of the invention is producible by, in a first process step, applying at least one clearcoat film I of a coating material I curable  
25 thermally and with actinic radiation to the surface of the substrate.

Accordingly, in the context of the present invention, it is possible to apply only one clearcoat film I of

the coating material I. However, two or more such clearcoat films I may be applied. In this case, different coating materials I may be employed to construct the clearcoat films I. In the majority of  
5 cases, however, the target properties profile of the clearcoat system A of the invention is achieved with one clearcoat film I.

The clearcoat film I is applied in a wet film thickness  
10 such that curing results, in the finished clearcoat system A of the invention, in a dry film thickness of from 10 to 100, preferably from 15 to 75, with particular preference from 20 to 55, and in particular from 20 to 35  $\mu\text{m}$ .

15 The application of the coating material I for the purpose of producing the clearcoat film I may take place by any customary application method, such as spraying, knife coating, brushing, flow coating, dipping  
20 or rolling, for example. Preference is given to using spray application methods, such as compressed air spraying, airless spraying, high-speed rotation, electrostatic spray application (ESTA), alone or in conjunction with hot spray application such as hot-air  
25 spraying, for example. The applications may be implemented at temperatures of max. 70 to 80° Celsius, so that appropriate application viscosities are achieved without any change or damage to the coating material I, or its overspray, which may be intended for

reprocessing, during the short period of thermal stress. For instance, hot spraying may be configured such that the coating material I is heated only very shortly in, or shortly before, the spray nozzle.

5

The spray booth used for the application may be operated, for example, with an optionally thermostatable recirculation system which is operated with an appropriate absorption medium for the  
10 overspray, an example of such a medium being the coating material I itself.

Application is preferably conducted under illumination with visible light with a wavelength of more than  
15 550 nm, or with light excluded. This prevents material change or damage to the coating material I or the overspray.

Of course, the above-described application methods may  
20 also be employed for the production of the clearcoat film II or the basecoat film III and also, if desired, further coating films, in the context of the processes A or B of the invention.

25 In accordance with the invention, the clearcoat film I is partially cured following its application. Viewed in terms of its methodology, the partial curing does not differ from the customary full curing of a coating film. In this case, crosslinking is carried out only

until the clearcoat film I possesses, on the one hand, a dimensional stability sufficient for the purposes of the processes A or B of the invention and, on the other hand, a sufficient amount of the crosslinkable functional groups (a11) and (a21) and/or (a12) and (a22) (complementary functional groups) described below for subsequent crosslinking and for intercoat adhesion. The extent of partial curing may therefore vary very widely and is guided by the requirements of each individual case. However, it may be determined by the skilled worker on the basis of his or her general knowledge in the art and/or on the basis of simple preliminary tests. Of the crosslinkable functional groups present in the coating material I, preferably from 0.5 to 99.5, with particular preference from 1 to 99, with very particular preference from 2 to 90, and in particular from 3 to 80 mol% are reacted. It is especially preferable if the clearcoat film I is still tacky following its partial curing.

20

In accordance with the invention, clearcoat film I may be partially cured with actinic radiation or thermally, or with actinic radiation and thermally. In accordance with the invention it is of advantage to cure the clearcoat film I partially with actinic radiation, since in this case it is possible to exert particularly effective control over the degree of crosslinking by way of the input of radiative energy.

Curing may take place after a certain rest period. This period may last for from 30 seconds to 2 hours, preferably for from 1 minute to 1 hour, and in particular for from 1 minute to 30 minutes. The rest  
5 period is used, for example, for leveling and for devolatilization of the clearcoat I or for the evaporation of volatile constituents such as solvents, water, or carbon dioxide if the coating material has been applied using supercritical carbon dioxide as  
10 solvent. The rest period may be assisted and/or shortened by the application of elevated temperatures up to 80° Celsius, provided this does not entail any damage or change to the clearcoat film I, such as premature complete crosslinking, for instance.

15 In accordance with the invention, curing with actinic radiation takes place with UV radiation or electron beams. If desired, it may be carried out, or supplemented, with actinic radiation from other  
20 sources. In the case of electron beams, it is preferred to operate under an inert gas atmosphere. This may be ensured, for example, by supplying carbon dioxide and/or nitrogen directly to the surface of the clearcoat film I.

25 In the case of curing with UV radiation as well it is possible to operate under inert gas in order to prevent the formation of ozone.

Curing with actinic radiation is carried out using the customary and known radiation sources and optical auxiliary measures. Examples of suitable radiation sources are high- or low-pressure mercury vapor lamps, with or without lead doping in order to open up a radiation window up to 405 nm, or electron beam sources. The arrangement of these emitters is known in principle and may be adapted to the circumstances of the workpiece and the process parameters. In the case of workpieces of complex shape such as automobile bodies, those regions not accessible to direct radiation (shadow regions) such as cavities, folds and other structural undercuts may be (partially) cured using pointwise, small-area or all-round emitters in conjunction with an automatic movement means for the irradiation of cavities or edges.

The equipment and conditions for these curing methods are described, for example, in R. Holmes, U.V. and E.B. Curing Formulations for Printing Inks, Coatings and Paints, SITA Technology, Academic Press, London, United Kingdom 1984.

The (partial) curing here may take place in stages, i.e., by multiple exposure to light or to actinic radiation. It may also take place alternately, i.e., by curing alternately with UV radiation and electron beams.



Thermal curing as well has no special features in terms of its method but instead takes place in accordance with the customary and known methods, such as heating in a forced air oven or irradiation with IR lamps. As  
5 with actinic radiation curing, thermal curing may also take place in stages. Thermal curing takes place advantageously at a temperature of from 50 to 100°C, with particular preference from 80 to 100°C, and in particular from 90 to 100°C for a period of from 1 min  
10 up to 2 h, with particular preference from 2 min up to 1 h, and in particular from 3 min to 30 min. Where the substrates used have a high capacity to withstand thermal stress, thermal crosslinking may be conducted even at temperatures above 100°C. In this case it is  
15 generally advisable for the temperatures used not to exceed 180°C, preferably 160°C, and in particular 140°C.

Where thermal curing and actinic radiation curing are  
20 employed together, these methods may be used simultaneously or in alternation. Where the two curing methods are used in alternation, it is possible, for example, to commence with thermal curing and to end with actinic radiation curing. In other cases it may  
25 prove advantageous to begin and to end with actinic radiation curing. The skilled worker is able to determine the curing method most advantageous for the case in hand on the basis of his or her general

knowledge in the art, possibly with the assistance of simple preliminary tests.

Of course, the curing methods described above may also be employed for the production of the clearcoat film II or the basecoat film III and also, if desired, further coating films in the context of the processes A or B of the invention.

10 The coating material I for use in accordance with the invention for the production of the clearcoat film I comprises at least one constituent (a1) containing at least two functional groups (a11) which serve for crosslinking with actinic radiation.

15 Examples of suitable functional groups (a11) are epoxide groups or olefinically unsaturated double bonds, as present in vinyl, allyl, cinnamoyl, methacryloyl or acryloyl groups, especially  
20 methacryloyl or acryloyl groups. As is known, the epoxide groups are used for cationic photopolymerization, whereas the olefinically unsaturated double bonds are primarily suitable for free-radical photopolymerization. In accordance with  
25 the invention, the constituent (a1) may contain epoxide groups and olefinic double bonds, so that it may be subjected to crosslinking with actinic radiation by both mechanisms. It is of advantage, however, to use

exclusively olefinically unsaturated double bonds of the abovementioned kind as functional groups (a11).

The constituent (a1) for use in accordance with the invention may further comprise at least one, preferably at least two functional group(s) (a12) which are able to undergo thermal crosslinking reactions with the complementary functional groups (a22) of the constituent (a2) described below.

10

Examples of suitable complementary functional groups (a12) and (a22) are evident from the overview below, in which R represents organic groups.

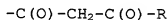
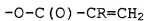
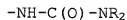
15 **Overview: Examples of complementary functional groups (a12) and (a22) in the**

**Constituent (a1) and Constituent (a2)**

**or**

**Constituent (a2) and Constituent (a1)**

-SH	-C(O)-OH
-NH <sub>2</sub>	-C(O)-O-C(O)-
-OH	-NCO
	-NH-C(O)-OR
	-CH <sub>2</sub> -OH
	-CH <sub>2</sub> -O-CH <sub>3</sub>
	-NH-C(O)-CH(-C(O)OR) <sub>2</sub>
	-NH-C(O)-CH(-C(O)OR)(-C(O)-R)



The selection of the respective complementary groups (a12) and (a22) is guided firstly by the consideration that they should not undergo any unwanted reactions initiated by actinic radiation or should not disrupt or inhibit the curing with actinic radiation, and secondly by the temperature range within which thermal curing is to take place. In this context it is of advantage in accordance with the invention, especially with regard to heat-sensitive substrates such as plastics, to choose a temperature range which does not go beyond 100°C, especially 80°C. In the light of these boundary conditions, hydroxyl groups and isocyanate groups have proven advantageous as complementary functional groups, and so are employed with preference in accordance with

the invention. Particular advantages result if the hydroxyl groups are used as functional groups (a12) and the isocyanate groups as functional groups (a22).

5 Where there is no functional group (a12) in the constituent (a1), the coating material I mandatorily includes at least one thermally curable constituent (a7), which is described in detail below.

10 Accordingly, the particularly advantageous constituent (a1) comprises an oligomeric or polymeric compound curable with actinic radiation or thermally which comprises, if desired, at least one, preferably at least two, and in particular at least three hydroxyl  
15 group(s) (a12) and at least two and especially three (meth)acryloyl groups (a11).

In the context of the present invention, an oligomeric compound is a compound containing in general on average  
20 from 2 to 15 repeating basic structures or monomer units. A polymeric compound, in contrast, is a compound containing in general on average at least 10 repeating basic structures or monomer units. Compounds of this kind are also referred to by those in the art as  
25 binders or resins.

In contradistinction thereto, a low molecular mass compound in the context of the present invention is a compound which derives substantially only from one

basic structure or one monomer unit. Compounds of this kind are generally referred to by those in the art as reactive diluents.

- 5 The polymers or oligomers used as binders (a1) normally have a number-average molecular weight of from 500 to 50 000, preferably from 1 000 to 5 000. They preferably have a double bond equivalent weight of from 400 to 2 000, with particular preference from 500 to 900.
- 10 Moreover, at 23°C, they preferably have a viscosity of from 250 to 11 000 mPas. They are employed preferably in an amount of from 5 to 90% by weight, with particular preference from 10 to 80% by weight, and in particular from 15 to 70% by weight, based in each case
- 15 on the overall amount of the coating material I.

Examples of suitable binders or resins (a1) come from the oligomer and/or polymer classes of the (meth)acryloyl-functional (meth)acrylic copolymers,

20 polyether acrylates, polyester acrylates, polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates and phosphazene acrylates and the corresponding methacrylates. It is preferred to use binders (a1) which are free from

25 aromatic structural units. Preference is therefore given to the use of urethane (meth)acrylates, phosphazene (meth)acrylates and/or polyester (meth)-acrylates, with particular preference urethane

(meth)acrylates, especially aliphatic urethane (meth)acrylates.

5 The urethane (meth)acrylates (a1) are obtained by reacting a diisocyanate or polyisocyanate with a chain extender from the group of the diols/polyols and/or diamines/polyamines and/or dithiols/polythiols and/or alkanolamines and subsequently reacting the remaining free isocyanate groups with at least one hydroxyalkyl  
10 (meth)acrylate or hydroxyalkyl ester of other ethylenically unsaturated carboxylic acids.

The amounts of chain extender, diisocyanate and/or polyisocyanate and hydroxyalkyl ester are in this case  
15 preferably chosen so that

1.) the ratio of equivalents of the NCO groups to the reactive groups of the chain extender (hydroxyl, amino and/or mercaptyl groups) is between 3:1 and  
20 1:2, preferably 2:1 and

2.) the OH groups of the hydroxyalkyl esters of the ethylenically unsaturated carboxylic acids are present in stoichiometric amount in relation to  
25 the remaining free isocyanate groups of the prepolymer formed from isocyanate and chain extender.

It is also possible to prepare the urethane (meth)acrylates (a1) by first reacting some of the isocyanate groups with a diisocyanate or polyisocyanate with at least one hydroxyalkyl ester and then reacting  
5 the remaining isocyanate groups with a chain extender. In this case as well the amounts of chain extender, isocyanate and hydroxyalkyl ester are chosen so that the ratio of equivalents of the NCO groups to the reactive groups of the chain extender is between 3:1  
10 and 1:2, preferably 2:1, and the ratio of equivalents of the remaining NCO groups to the OH groups of the hydroxyalkyl ester is 1:1. Of course, all intermediate forms between these two processes are also possible. For example, some of the isocyanate groups of a  
15 diisocyanate may first be reacted with a diol, after which a further portion of the isocyanate groups may be reacted with the hydroxyalkyl ester, and, subsequently, the remaining isocyanate groups may be reacted with a diamine.

20

These various preparation processes of the urethane (meth)acrylates (a1) are known (cf., e.g., EP-A-204 161).

25 Flexibilization of the urethane (meth)acrylates (a1) is possible, for example, by reacting corresponding isocyanate-functional prepolymers or oligomers with relatively long-chain aliphatic diols and/or diamines, especially aliphatic diols and/or diamines having at



least 6 carbon atoms. This flexibilization reaction may be carried out before or after the addition of acrylic or methacrylic acid onto the oligomers or prepolymers.

5 Examples of suitable urethane (meth)acrylates (a1) that may be mentioned include the following, commercially available, polyfunctional aliphatic urethane acrylates:

- 10 - Crodamer® UVU 300 from Croda Resins Ltd, Kent, United Kingdom;
- Genomer® 4302, 4235, 4297 or 4316 from Rahn Chemie, Switzerland;
- Ebecryl® 284, 294, IRR351, 5129 or 1290 from UCB, Drogenbos, Belgium;
- 15 - Roskydal® LS 2989 or LS 2545 or V94-504 from Bayer AG, Germany;
- Viaktin® VTE 6160 from Vianova, Austria; and
- Laromer® 8861 from BASF AG, and experimental products derived therefrom by modification.

20

An example of a suitable phosphazene (meth)acrylate (a1) is the phosphazene dimethacrylate from Idemitsu, Japan.

25 The coating material I of the invention further comprises a constituent (a2).

This constituent (a2) also comprises a resin as defined above for the description of the resins (a1).

Accordingly, the resins (a2) also come from the oligomer and polymer classes described above. Of advantage in this context are the (meth)acryloyl-functional (meth)acrylic copolymers, which are  
5 therefore used with preference in accordance with the invention as resins (a2).

The resins (a2) are employed in an amount of preferably from 5 to 90% by weight, with particular preference  
10 from 10 to 80% by weight, and in particular from 15 to 70% by weight, based in each case on the overall amount of the coating material I.

The resins (a2) contain at least two, in particular at  
15 least three functional groups (a21) which serve for crosslinking with actinic radiation. Examples of suitable functional groups (a21) for use in accordance with the invention are the functional groups (a11) described above.

20

The resins (a2) further comprise at least one, preferably at least two and in particular at least three functional group(s) (a22) which serve for thermal crosslinking. Examples of suitable such functional  
25 groups may be taken from the above overview. Isocyanate groups are particularly advantageous in this context and are therefore used with very particular preference in accordance with the invention as functional groups (a22). Particular advantages result if the resins (a2)

have an isocyanate group (a22) content of from 7 to 20% by weight, with particular preference from 8 to 18% by weight, and in particular from 9 to 17% by weight, based in each case on the resin (a2).

5

Examples of suitable resins (a2) of the type described above are described, for example, in the patents US-A-5 234 970, EP-A-0 549 116, and EP-A-0 618 244.

- 10 The coating material I for use in accordance with the invention may comprise at least one photoinitiator (a3). If the coating material I or the clearcoat film I is to be crosslinked with UV radiation, the use of a photoinitiator (a3) is generally necessary. Where they
- 15 are used, they are present in the coating material I preferably in fractions of from 0.1 to 10% by weight, from 1 to 8% by weight, and in particular from 2 to 6% by weight, based in each case on the overall amount of the coating material I.

20

- Examples of suitable photoinitiators are those of the Norrish II type, whose mechanism of action is based on an intramolecular variant of the hydrogen abstraction reactions which occur diversely in photochemical
- 25 reactions (reference may be made here, by way of example, to Römpp Chemie Lexikon, 9th, expanded and revised edition, Georg Thieme Verlag, Stuttgart, Vol. 4, 1991) or cationic photoinitiators (reference may be made here, by way of example, to Römpp Lexikon Lacke

und Druckfarben, Georg Thieme Verlag, Stuttgart, 1998, pages 444 to 446), especially benzophenones, benzoin ethers, or phosphine oxides. It is also possible, for example, to use the products available commercially under the names Irgacure® 184, Irgacure® 1800 and Irgacure® 500 from Ciba Geigy, Grenocure® MBF from Rahn, and Lucirin® TPO from BASF AG.

10 In addition to the photoinitiators (a3), it is possible to use customary sensitizers such as anthracene in effective amounts.

Furthermore, the coating material I may comprise at least one thermal crosslinking initiator (a4). At from 15 80 to 120°C, these initiators form free radicals which start the crosslinking reaction. Examples of thermally labile free-radical initiators are organic peroxides, organic azo compounds or C-C-cleaving initiators such as dialkyl peroxides, peroxocarboxylic acids, 20 peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azo dinitriles, or benzpinacol silyl ethers. Particular preference is given to C-C-cleaving initiators, since their thermal cleavage does not produce any gaseous decomposition products which might 25 lead to defects in the coating film. Where used, their amounts are generally from 0.1 to 10, preferably from 0.5 to 8, and in particular from 1 to 5% by weight, based in each case on the overall amount of the coating material I.

Moreover, the coating material I may comprise at least one reactive diluent (a5) curable thermally and/or with actinic radiation.

- 5 Examples of suitable thermally crosslinkable reactive diluents (a5) are oligomeric polyols obtainable from oligomeric intermediates themselves obtained by metathesis reactions from acyclic monoolefins and cyclic monoolefins, by hydroformylation and subsequent  
10 hydrogenation.

Examples of suitable cyclic monoolefins are cyclobutene, cyclopentene, cyclohexene, cyclooctene, cycloheptene, norbornene or 7-oxanorbornene.

- 15 Examples of suitable acyclic monoolefins are present in hydrocarbon mixtures obtained in petroleum processing by cracking (C<sub>5</sub> cut).

- 20 Examples of suitable oligomeric polyols (a5) for use in accordance with the invention have a hydroxyl number (OHN) of from 200 to 450, a number-average molecular weight Mn of from 400 to 1 000, and a mass-average molecular weight Mw of from 600 to 1 100.

- 25 Further examples of suitable thermally crosslinkable reactive diluents (a5) are hyperbranched compounds containing a tetrafunctional central group, derived from ditrimethylolpropane, diglycerol, ditrimethylol-

ethane, pentaerythritol, tetrakis(2-hydroxyethyl)-methane, tetrakis(3-hydroxypropyl)methane or 2,2-bishydroxymethyl-1,4-butanediol (homopentaerythritol). These reactive diluents may be prepared in accordance  
5 with the customary and known methods of preparing hyperbranched and dendrimeric compounds. Suitable synthesis methods are described, for example, in the patents WO 93/17 060 and WO 96/12 754 or in the book by G.R. Newkome, C.N. Moorefield and F. Vögtle, "Dendritic  
10 Molecules, Concepts, Syntheses, Perspectives", VCH, Weinheim, New York, 1996.

Further examples of suitable reactive diluents (a5) are polycarbonatediols, polyesterpolyols, poly(meth)-  
15 acrylatediols, and hydroxyl-containing polyadducts.

Examples of suitable reactive solvents which may be used as reactive diluents (a5) are butyl glycol, 2-methoxypropanol, n-butanol, methoxybutanol,  
20 n-propanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, trimethylol-  
25 propane, ethyl 2-hydroxypropionate and 3-methyl-3-methoxybutanol, and also derivatives based on propylene glycol, e.g., ethoxyethyl propionate, isopropoxypropanol or methoxypropyl acetate.

Examples of reactive diluents (a5) used that may be crosslinked with actinic radiation are (meth)acrylic acid and esters thereof, maleic acid and its esters, including monoesters, vinyl acetate, vinyl ethers, vinylureas, and the like. Examples that may be mentioned include alkylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, vinyl (meth)acrylate, allyl (meth)-acrylate, glycerol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylol-propane di(meth)-acrylate, styrene, vinyltoluene, divinylbenzene, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipropylene glycol di(meth)acrylate, hexanediol di(meth)acrylate, ethoxyethoxyethyl acrylate, N-vinylpyrrolidone, phenoxyethyl acrylate, dimethylaminoethyl acrylate, hydroxyethyl (meth)-acrylate, butoxyethyl acrylate, isobornyl (meth)-acrylate, dimethylacrylamide, and dicyclopentyl acrylate, and also the long-chain linear diacrylates described in EP-A-0 250 631 and having a molecular weight of from 400 to 4 000, preferably from 600 to 2 500. The two acrylate groups may, for example, be separated by a polyoxybutylene structure. Further candidates for use are 1,12-dodecyl diacrylate and the reaction product of 2 mol of acrylic acid with one mole of a dimeric fatty alcohol having generally 36 carbon atoms. Mixtures of the abovementioned monomers are also suitable.

Preferred for use as reactive diluents (a5) are mono- and/or diacrylates, such as isobornyl acrylate, hexanediol diacrylate, tripropylene glycol diacrylate, Laromer® 8887 from BASF AG, and Actilane® 423 from  
5 Akcros Chemicals Ltd., UK, for example. Particular preference is given to the use of isobornyl acrylate, hexanediol diacrylate, and tripropylene glycol diacrylate.

10 Where used, the reactive diluents (a5) are employed in an amount of preferably from 2 to 70, with particular preference from 10 to 65, and in particular from 15 to 50% by weight, based in each case on the overall amount of the coating material I.

15 The coating material may further comprise one or more customary coatings additives (a6) in effective amounts, i.e., in amounts of preferably up to 20% by weight, with particular preference up to 15% by weight, and in  
20 particular up to 10% by weight, based in each case on the overall amount of the coating material I.

Examples of suitable coatings additives (a6) are

25 - UV absorbers;

- light stabilizers such as HALS compounds, benzotriazoles or oxalanilides;



- free-radical scavengers;
- crosslinking catalysts such as dibutyltin dilaurate or lithium decanoate;
- slip additives;
- 5 - polymerization inhibitors;
- defoamers;
- emulsifiers, especially nonionic emulsifiers such as alkoxylated alkanols and polyols, phenols and alkylphenols or anionic emulsifiers such as alkali metal salts or ammonium salts of alkanecarboxylic acids, 10 alkanesulfonic acids, and sulfo acids of alkoxylated alkanols and polyols, phenols and alkylphenols;
- wetting agents such as siloxanes, fluorine compounds, carboxylic monoesters, phosphoric esters, polyacrylic acids and their copolymers, or polyurethanes; 15
- adhesion promoters such as tricyclodecanedimethanol;
- leveling agents;
- film-forming auxiliaries such as cellulose derivatives;
- transparent pigments such as silica;
- 20 - flame retardants; or

- flattening agents.

Further examples of suitable coatings additives (a6) are described in the textbook "Lackadditive" [Additives for coatings] by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

Not least, the coating material I may comprise at least one thermally curable constituent (a7) in minor amounts. In the context of the present invention, "minor amounts" are amounts which do not adversely affect the dual-cure properties of the coating material I but instead vary them advantageously. Where used, their proportion in the coating material I should not exceed generally 40% by weight, preferably 35% by weight, and especially 30% by weight.

Examples of suitable constituents (a7) are the binders and crosslinking agents known from the thermally curable coating materials.

20

Examples of suitable binders (a7) are linear and/or branched and/or block, comb and/or random poly(meth)acrylates or acrylate copolymers, polyesters, alkyds, amino resins, polyurethanes, polylactones, polycarbonates, polyethers, epoxyresin-amine adducts, (meth)acrylatediols, partially saponified polyvinyl esters or polyureas, of which the acrylate copolymers,

25

the polyesters, the polyurethanes, the polyethers, and the epoxyresin-amine adducts are advantageous.

Suitable binders (a7) are sold, for example, under the  
5 trade names Desmophen® 650, 2089, 1100, 670, 1200 and  
2017 by Bayer, under the trade names Priplas and  
Pripol® by Uniqema, under the trade names Chempol®  
polyester or polyacrylate-polyol by CCP, under the  
trade names Crodapol® 0-85 and 0-86 by Croda, or under  
10 the trade name Formrez® ER417 by Witco.

Examples of suitable crosslinking agents (a7) are  
blocked diisocyanates and/or polyisocyanates.

15 Examples of suitable diisocyanates and/or poly-  
isocyanates for preparing the block derivatives (a7)  
are organic polyisocyanates, especially so-called paint  
polyisocyanates, having free isocyanate groups attached  
to aliphatic, cycloaliphatic, araliphatic and/or  
20 aromatic moieties. Preference is given to polyiso-  
cyanates having from 2 to 5 isocyanate groups per  
molecule and viscosities of from 100 to 10 000,  
preferably from 100 to 5 000, and in particular from  
100 to 2 000 mPas (at 23°C). If desired, small amounts  
25 of organic solvent, preferably from 1 to 25% by weight  
based on straight polyisocyanate, may be added to the  
polyisocyanates in order to make it easier to  
incorporate the isocyanate and, if appropriate, to  
reduce the viscosity of the polyisocyanate to a level

within the abovementioned ranges. Examples of suitable solvent additives to the polyisocyanates are ethoxyethyl propionate, amyl methyl ketone, and butyl acetate. Furthermore, the polyisocyanates may have been  
5 hydrophilically or hydrophobically modified in a customary and known manner.

Examples of suitable polyisocyanates are described, for example, in "Methoden der organischen Chemie", Houben-  
10 Weyl, Volume 14/2, 4th Edition, Georg Thieme Verlag, Stuttgart, 1963, pages 61 to 70, and by W. Siefken, Liebigs Annalen der Chemie, Volume 562, pages 75 to 136. Suitable examples are the polyurethane prepolymers containing isocyanate groups that can be prepared by  
15 reacting polyols with an excess of polyisocyanates and are preferably of low viscosity.

Further examples of suitable polyisocyanates are polyisocyanates containing isocyanurate, biuret,  
20 allophanate, iminooxadiazinedione, urethane, urea and/or uretdione groups. Polyisocyanates containing urethane groups, for example, are prepared by reacting some of the isocyanate groups with polyols, such as trimethylolpropane and glycerol, for example.  
25 Preference is given to the use of aliphatic or cycloaliphatic polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane

2,4'-diisocyanate, dicyclohexylmethane 4,4'-diisocyanate, or 1,3-bis(isocyanatomethyl)cyclohexane, diisocyanates derived from dimeric fatty acids, as sold under the commercial designation DDI 1410 by Henkel,  
5 1,8-diisocyanato-4-isocyanatomethyloctane, 1,7-diisocyanato-4-isocyanatomethylheptane or 1-isocyanato-2-(3-isocyanatopropyl)cyclohexane, or mixtures of these polyisocyanates.

10 Very particular preference is given to using mixtures of polyisocyanates containing uretdione and/or isocyanurate and/or allophanate groups, based on hexamethylene diisocyanate, as formed by catalytic oligomerization of hexamethylene diisocyanate using  
15 appropriate catalysts. The polyisocyanate constituent may further comprise any desired mixtures of the free polyisocyanates exemplified.

Examples of suitable blocking agents are the blocking  
20 agents known from the U.S. patent US-A-4 444 954, such as

i) phenols such as phenol, cresol, xylenol, nitrophenol, chlorophenol, ethylphenol, t-butylphenol, hydroxybenzoic acid, esters of this acid,  
25 or 2,5-di-tert-butyl-4-hydroxytoluene;

ii) lactams, such as  $\epsilon$ -caprolactam,  $\delta$ -valerolactam,  $\gamma$ -butyrolactam or  $\beta$ -propiolactam;

- iii) active methylenic compounds, such as diethyl malonate, dimethyl malonate, ethyl or methyl acetoacetate, or acetylacetone;
- 5 iv) alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, n-amyl alcohol, t-amyl alcohol, lauryl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, 10 diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, propylene glycol monomethyl ether, methoxymethanol, glycolic acid, glycolic esters, lactic acid, lactic esters, methylolurea, methylolmelamine, diacetone alcohol, 15 ethylenechlorohydrin, ethylenebromohydrin, 1,3-dichloro-2-propanol, 1,4-cyclohexyldimethanol or acetocyanohydrin;
- 20 v) mercaptans such as butyl mercaptan, hexyl mercaptan, t-butyl mercaptan, t-dodecyl mercaptan, 2-mercaptobenzothiazole, thiophenol, methylthiophenol or ethylthiophenol;
- 25 vi) acid amides such as acetoanilide, acetoanisidinamide, acrylamide, methacrylamide, acetamide, stearamide or benzamide;
- vii) imides such as succinimide, phthalimide or maleimide;

viii) amines such as diphenylamine, phenylnaphthylamine, xylylidine, N-phenylxylylidine, carbazole, aniline, naphthylamine, butylamine, dibutylamine or butylphenylamine;

5

ix) imidazoles such as imidazole or 2-ethylimidazole;

x) ureas such as urea, thiourea, ethyleneurea, ethylenethiourea or 1,3-diphenylurea;

10

xi) carbamates such as phenyl N-phenylcarbamate or 2-oxazolidone;

xii) imines such as ethyleneimine;

15

xiii) oximes such as acetone oxime, formaldoxime, acetaldoxime, acetoxime, methyl ethyl ketoxime, diisobutyl ketoxime, diacetyl monoxime, benzophenone oxime or chlorohexanone oximes;

20

xiv) salts of sulfurous acid such as sodium bisulfite or potassium bisulfite;

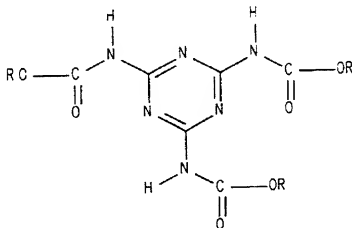
25

xv) hydroxamic esters such as benzyl methacrylohydroxamate (BMH) or allyl methacrylohydroxamate; or

xvi) substituted pyrazoles, ketoximes, imidazoles or triazoles; and also

mixtures of these blocking agents, especially dimethylpyrazole and triazoles, malonic esters and acetoacetic esters or dimethylpyrazole and succinimide.

- 5 As crosslinking agent (a7) it is also possible to use tris(alkoxycarbonylamino)triazines of the general formula 5



10

- Examples of suitable tris(alkoxycarbonylamino)-triazines (a7) are described in the patents US-A-4 939 213, US-A-5 084 541, and EP-A-0 624 577. Use is made in particular of the tris(methoxy-, tris-  
15 (butoxy- and/or tris(2-ethylhexoxycarbonylamino)triazines.

- The methyl butyl mixed esters, the butyl 2-ethylhexyl mixed esters, and the butyl esters are of advantage.  
20 They have the advantage over the straight methyl ester of better solubility in polymer melts, and also have less of a tendency to crystallize out.



In particular as crosslinking agents (a7) it is possible to use amino resins, examples being melamine resins. Any amino resin suitable for transparent topcoats or clearcoats, or a mixture of such amino  
5 resins, may be used. Especially suitable are the customary and known amino resins some of whose methylol and/or methoxymethyl groups have been defunctionalized by means of carbamate or allophanate groups. Crosslinking agents of this kind are described in the  
10 patents US-A-4 710 542 and EP-B-0 245 700 and also in the article by B. Singh and coworkers, "Carbamylmethylated Melamines, Novel Crosslinkers for the Coatings Industry" in Advanced Organic Coatings Science and Technology Series, 1991, Volume 13, pages 193 to 207.  
15 Moreover, the amino resins may also be used as binders (a1) in the base paint (A1).

Further examples of suitable crosslinking agents (a7) are beta-hydroxyalkylamides such as N,N,N',N'-tetrakis-  
20 (2-hydroxyethyl)adipamide or N,N,N',N'-tetrakis(2-hydroxypropyl)adipamide.

Further examples of suitable crosslinking agents (a7) are siloxanes, especially siloxanes containing at least  
25 one trialkoxy- or dialkoxysilane group.

Further examples of suitable crosslinking agents (a7) are polyanhydrides, especially polysuccinic anhydride.

If the coating material I includes a resin (a1) containing no functional groups (a12), the constituent (a7) is mandatorily present in the coating material I. In accordance with the invention, it is of advantage in  
5 this case if the above-described binders (a7) are used for this purpose.

All in all, it is of advantage for the coating material of the invention if the complementary functional groups  
10 (a12) and (a22), especially hydroxyl groups and the isocyanate groups, are present in a molar ratio OH/NCO of from 0.5 to 2:1, with particular preference from 0.8 to 1.5:1, with very particular preference from 0.8 to 1.2:1, and in particular from 0.8 to 1.0:1.

15 The coating material I for use in accordance with the invention may be present in different forms. For instance, given an appropriate choice of its above-described constituents, it may be present as a liquid  
20 coating material I which is essentially free from organic solvents and/or water. However, the coating material I may also comprise a solution or dispersion of the above-described constituents in water and/or organic solvents. Furthermore, the coating material I,  
25 given an appropriate choice of its above-described constituents, may be a powder clearcoat material I. This powder clearcoat material I may be dispersed if desired in water, so giving a powder slurry clearcoat material I. If the reactivity of its constituents (a1)

and/or (a7) on the one hand and (a2) on the other permits, the coating material I may be a one-component system. If, however, there is a risk of the abovementioned constituents undergoing premature thermal crosslinking, it is advisable to configure the coating material I as a two-component or multicomponent system, in which at least the constituent (a2) is stored separately from the remaining constituents and is not added to them until shortly before use.

In the second process step, a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally is applied to the partially cured clearcoat film I.

The coating material II may also be present as a liquid, solution, dispersion, powder clearcoat material or powder slurry clearcoat material I. It is applied using the methods described above for the coating material I. It is of advantage in accordance with the invention to apply the coating material II in a wet film thickness such that, after curing, the clearcoat II in the clearcoat system A of the invention has a dry film thickness of preferably from 2 to 15, with particular preference from 3 to 10, and in particular from 4 to 8  $\mu\text{m}$ .

The substantial constituents of the coating material II are nanoparticles, especially those based on silicon

dioxide, aluminum oxide and zirconium oxide. They have a particle size of less than 50 nm, and have no flattening effect. Preferably, nanoparticles based on aluminum oxide and zirconium oxide are used.

5

Examples of suitable nanoparticles based on silicon dioxide are pyrogenic silicas, which are sold under the trade name Aerosil® VP8200, VP721 or R972 by Degussa or under the trade names Cab O Sil® TS 610, CT 1110F or

10 CT 1110G by Cabot.

In general, these nanoparticles are sold in the form of dispersions in monomers curable with actinic radiation, such as the reactive diluents (a5) described above.

15 Examples of suitable monomers which are especially suitable for the present application are alkoxyolated pentaerythritol tetraacrylate or triacrylate, ditrimethylolpropane tetraacrylate or triacrylate, dineopentyl glycol diacrylate, trimethylolpropane  
20 triacrylate, trishydroxyethyl isocyanurate triacrylate, dipentaerythritol pentaacrylate or hexaacrylate, or hexanediol diacrylate. In general, these dispersions contain the nanoparticles in an amount, based in each case on the dispersions, of from 10 to 80% by weight,  
25 preferably from 15 to 70% by weight, with particular preference from 20 to 60% by weight, and in particular from 25 to 50% by weight.

An example of a nanoparticle dispersion which is especially suitable in accordance with the invention is the dispersion sold under the trade name High Link® OG 103-31 by Clariant Hoechst.

5

The nanoparticle dispersions are present in the coating material II advantageously in an amount of from 2 to 30% by weight, with particular preference from 3 to 25% by weight, and in particular from 5 to 20% by weight, based in each case on the overall amount of the coating material II.

The coating material II further comprises a resin curable with actinic radiation. Examples of suitable resins curable with actinic radiation come from the oligomer and polymer classes which are described above in connection with the resin (a1). It is of advantage in accordance with the invention if the resins used in the coating material II have no functional groups (a2) or (a22). Of these resins, the urethane (meth)acrylates and the (meth)acrylate oligomers have particular advantages and are therefore used with particular preference in accordance with the invention.

25 The resin is employed advantageously in an amount of from 5 to 90% by weight, with particular preference from 10 to 80% by weight, and in particular from 20 to 70% by weight, based in each case on the overall amount of the coating material II.

Furthermore, the coating material II may include the constituents (a3), (a4), (a5), (a6) and/or (a7) described above in connection with the coating material I, in the amounts specified there.

5

In a procedure in accordance with the invention, the clearcoat films I and II are cured conjointly with actinic radiation and thermally in the process step 3. Here too, the apparatus and methods described above in  
10 connection with the partial curing of the clearcoat film I are employed.

In the alternative process A of the invention, which has particular advantages for automotive refinish in  
15 particular, the applied clearcoat film(s) I are cured not partially but completely in the first process step, using the apparatus and methods described above. Subsequently, the outer surface of the clearcoat film(s) I is roughened. The customary and known  
20 roughening methods, such as rubbing with sandpaper or steel wool, or filing or brushing, are appropriate in this case. Thereafter, in the second process step, the above-described clearcoat film II is applied and is cured with actinic radiation and also, if desired,  
25 thermally, again using the apparatus and methods described above.

The clearcoats A of the invention described above, which are preferably produced with the aid of the

processes A of the invention, may also be part of the multicoat systems B of the invention. Advantageously, these systems are produced with the aid of the processes B of the invention.

5

For this purpose, the clearcoat film(s) I in the first process step is or are applied not to the primed or unprimed substrates but rather to at least one color and/or effect basecoat film III which is present thereon, comprising a pigmented coating material III curable thermally and also, if desired, with actinic radiation.

In accordance with the invention it is of advantage to apply the clearcoat film(s) I by the wet-on-wet technique to the dried or flashed off, but not cured, basecoat film III.

Thereafter, in a first variant of the process B of the invention, the basecoat film(s) III and the clearcoat film(s) I are partly cured. Subsequently, in the third process step, the clearcoat film II is applied, after which the basecoat film(s) III, clearcoat film(s) I and clearcoat film II are cured conjointly with actinic radiation and thermally.

In the second variant of the process B of the invention, in the third process step the basecoat film(s) III and the clearcoat film(s) I are fully

cured, after which in the fourth process step the outer surface of the clearcoat film(s) I is roughened. Thereafter, in the fifth process step, the clearcoat film II is applied and in the sixth process step it is  
5 fully cured.

Suitable coating material III for the production of the basecoat film III comprises the customary and known basecoat materials, especially waterborne basecoat  
10 materials.

Examples of suitable waterborne basecoat materials are known from the patents EP-A-0 089 497, EP-A-0 256 540, EP-A-0 260 447, EP-A-0 297 576, WO 96/12 747,  
15 EP-A-0 523 610, EP-A-0 228 003, EP-A-0 397 806, EP-A-0 574 417, EP-A-0 531 510, EP-A-0 581 211, EP-A-0 708 788, EP-A-0 593 454, DE-A-43 28 092, EP-A-0 299 148, EP-A-0 394 737, EP-A-0 590 484, EP-A-0 234 362, EP-A-0 234 361, EP-A-0 543 817,  
20 WO 95/14 721, EP-A-0 521 928, EP-A-0 522 420, EP-A-0 522 419, EP-A-0 649 865, EP-A-0 536 712, EP-A-0 596 460, EP-A-0 596 461, EP-A-0 584 818, EP-A-0 669 356, EP-A-0 634 431, EP-A-0 678 536, EP-A-0 354 261, EP-A-0 424 705, WO 97/49 745,  
25 WO 97/49 747, EP-A-0 401 565, EP-B-0 730 613, and WO 95/14 721.

In the case of the processes B of the invention it is possible - as already mentioned - to employ all



application, curing and roughening methods and apparatus described above in connection with the coating material I.

5 Owing to their glasslike surface, the clearcoats A of the invention and the multicoat systems B of the invention have an extremely high scratch resistance. This advantageous property is supplemented by an outstanding optical properties profile and also  
10 outstanding weathering stability and chemical resistance. As a result, motor vehicles, plastics parts, furniture and other parts for private or industrial use, including coils and containers, which comprise at least one clearcoat A of the invention  
15 and/or at least one multicoat system B of the invention, are superior in their value, their service properties and their service life to products which comprise only conventional coatings.

20 **Examples 1 and 2 and comparative experiment C1**

**The production of inventive clearcoat systems A (examples 1 and 2) and also a noninventive clearcoat system (comparative experiment C1)**

25

In the case of examples 1 and 2 and in the case of the comparative experiment C1, a clearcoat film I of a coating material I was applied to PMMA test panels, was predried for 6 minutes and was partially cured using UV

radiation with an energy of 1 or 2 millijoules/cm<sup>2</sup>. In all cases, the clearcoat film I was applied in a wet film thickness such that in the fully cured clearcoats of examples 1 and 2 and of the comparative experiment

5 C1 the resulting dry film thickness was from 25 to 27 µm.

The coating material I consisted of 100 parts by weight of a urethane (meth)acrylate which was free from

10 hydroxyl groups (Ebecryl® 5129 from UCB), 100 parts by weight of a polyesterpolyol (Desmophen® from Bayer AG), 2.5 parts by weight of a commercial photoinitiator (Irgacure® 819 from Ciba and Lucirin® TPO from BASF AG), 0.6 part by weight of a commercial UV absorber and

15 light stabilizer (mixture of Tinuvin® 400 and neutral HALS from Ciba and also a sterically hindered phenol) and 50 parts by weight of a commercial oligomeric acrylate containing free isocyanate groups and acrylate groups (Roskydal® 2545 from Bayer AG). For application,

20 the coating material I was adjusted to spray viscosity using a suitable organic solvent (mixture of butyl acetate, n-butanol and Ektapro®).

The coating material II was applied over the partially

25 cured clearcoat film I, in a wet clearcoat film thickness II such that complete curing resulted in a dry film thickness of from 4 to 6 µm.

In the case of example 1, the coating material II consisted of 30 parts by weight of a commercial (meth)acrylate oligomer (Ebecryl® IRR351 from UCB), 10 parts by weight of a commercial reactive diluent  
5 (Servocure® RTT 192 from Servo Delden), 10 parts by weight of a commercial dispersion of nanoparticles in a polyfunctional monomer (High Link® OG 103-31 from Clariant Hoechst), 2 parts by weight of a commercial photoinitiator (Lucirin® TPO from BASF AG), 1 part by  
10 weight of a commercial UV absorber (Cyagard 1164L from Cytec), and 0.05 part by weight of a commercially customary, siloxane-based wetting agent. For application, the coating material I was adjusted to spray viscosity (solids content about 30 to 40% by  
15 weight) using an appropriate organic solvent (mixture of butyl acetate, n-butanol and Ektapro®).

The coating material II of example 2 corresponded to that of example 1 except that in this case an  
20 additional 10 parts by weight of silica (Aerosil®) were present.

The coating material II of the comparative experiment C1 corresponded to the coating material of example 1  
25 except that in this case no High Link® OG 103-31 was present.

In examples 1 and 2 and in the comparative experiment C1, the clearcoat films I and II were fully cured,

following a rest period of 6 minutes at from 50 to 60°C, with UV radiation (from 1 to 3 joules/cm<sup>2</sup>) and thermally (10 minutes at 90°C).

- 5 The clearcoats were subjected to the Taber 5131 abrasion test with 100 and 500 cycles with a load of one kilogram per arm. Appropriate equipment is available from ERICHSEN, F-92508 Rueil-Malmaison, Cedex, France. After the test, the haze was determined
- 10 in accordance with DIN 67530. For comparison, the abrasion resistance of uncoated PMMA and PC plastic panels was measured. The table gives an overview of the results obtained. The comparison of the haze values in the table demonstrates the superior scratch resistance
- 15 of the clearcoats A of the invention, which are outstandingly suitable for imparting scratch resistance to sensitive surfaces of plastic.

Table: The haze values (losses in light transmissivity, in percent) of the inventive (examples 1 and 2) and the noninventive (comparative experiment C1) clearcoats

5

Example or comparative experiment no.	Loss of light transmissivity after:	
	100 cycles (%)	500 cycles (%)
C1	8	22
1	4	11
2	3	9
PMMA (for comparison)	30	41
PC (for comparison)	46	59

Additionally, the inventive clearcoats of examples 1 and 2 were subjected to the key test, which is relevant for everyday practice. For this purpose, they were scored under load with a BIC® pen having a ball of 2 mm in diameter. Here it was found that the inventive clearcoats were scratchable only at loads above 2 000 g. The corresponding load in the case of the siloxane-containing baking clearcoat, used as standard in this test, is 500 g.

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## What is claimed is:

1. A highly scratch-resistant multicoat clearcoat  
system A for a primed or unprimed substrate,  
5 producible by
  - (1) applying at least one clearcoat film I of a  
coating material I curable thermally and with  
actinic radiation to the surface of the  
10 substrate, and partially curing it, and
  - (2) applying a further clearcoat film II of a  
coating material II curable with actinic  
radiation and also, if desired, thermally,  
15 comprising nanoparticles, to the surface of  
the clearcoat film(s) I, and then
  - (3) curing the clearcoat films I and II  
conjointly with actinic radiation and  
20 thermally.
2. A highly scratch-resistant multicoat clearcoat  
system A for a primed or unprimed substrate,  
25 producible by
  - (1) applying at least one clearcoat film I of a  
coating material I curable thermally and with  
actinic radiation to the surface of the  
substrate, curing it and roughening it,

(2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

(3) curing the clearcoat film II with actinic radiation and, if desired, thermally.

10 3. A highly scratch-resistant, multicoat color and/or effect coating system B for a primed or unprimed substrate, producible by

15 (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,

20 (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially

25 curing them, and

(3) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally,

comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

5 (4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

10 4. A highly scratch-resistant multicoat color and/or effect coating system B for a primed or unprimed substrate, producible by

15 (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,

20 (2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III,

25 (3) curing the basecoat film III and clearcoat film(s) I conjointly, thermally and with actinic radiation,

(4) roughening the outer surface of the clearcoat film(s) I,



(5) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then

(6) curing the clearcoat film II with actinic radiation and, if desired, thermally.

10 5. A process for producing a highly scratch-resistant multicoat clearcoat system (A) on a primed or unprimed substrate, which comprises

15 (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, and partially curing it, and

20 (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

25 (3) curing the clearcoat films I and II conjointly with actinic radiation and thermally.

6. A process for producing a highly scratch-resistant multicoat clearcoat system A on a primed or unprimed substrate, which comprises

- 5 (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, curing it and roughening it,
- 10 (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the outer surface of the clearcoat film(s) I, and then
- 15 (3) curing the clearcoat film II with actinic radiation and, if desired, thermally.

7. A process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, which comprises

- 20 (1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if
- 25 desired, with actinic radiation to the surface of the substrate and drying it without curing,

(2) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation wet-on-wet to the surface of the basecoat film III, and partially curing them, and

(3) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then

(4) curing the basecoat film(s) III and the clearcoat films I and II conjointly with actinic radiation and thermally.

8. A process for producing a highly scratch-resistant multicoat color and/or effect coating system B on a primed or unprimed substrate, which comprises

(1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and also, if desired, with actinic radiation to the surface of the substrate and drying it without curing,

(2) applying at least one clearcoat film I of a coating material I curable thermally and with

actinic radiation wet-on-wet to the surface  
of the basecoat film III,

5 (3) curing the basecoat film III and clearcoat  
film(s) I conjointly, thermally and with  
actinic radiation,

10 (4) roughening the outer surface of the clearcoat  
film(s) I,

15 (5) applying a further clearcoat film II of a  
coating material II curable with actinic  
radiation and also, if desired, thermally,  
comprising nanoparticles, to the outer  
surface of the clearcoat film(s) I, and then

(6) curing the clearcoat film II with actinic  
radiation and, if desired, thermally.

20 9. The clearcoat system A as claimed in claim 1 or 2,  
the multicoat system B as claimed in claim 3 or 4,  
the process for producing the clearcoat system A  
as claimed in claim 5 or 6, or the process for  
producing the multicoat system B as claimed in  
25 claim 7 or 8, wherein the coating material II  
comprises nanoparticles based on silicon dioxide,  
aluminum oxide and zirconium oxide.

10. The clearcoat system A as claimed in any of claims  
1, 2 and 9, the multicoat system B as claimed in  
any of claims 3, 4 and 9, the process for  
producing the clearcoat system A as claimed in any  
5 of claims 5, 6 and 9, or the process for producing  
the multicoat system B as claimed in any of claims  
7 to 9, wherein the coating material I comprises

(a1) at least one constituent containing

10

(a11) at least two functional groups which serve  
for crosslinking with actinic radiation, and  
if desired

15

(a12) at least one functional group which is able  
to undergo thermal crosslinking reactions  
with a complementary functional group (a22)  
in the constituent (a2),

20

and

(a2) at least one constituent containing

25

(a21) at least two functional groups which serve  
for crosslinking with actinic radiation, and

(a22) at least one functional group which is able  
to undergo thermal crosslinking reactions

with a complementary functional group (a12)  
in the constituent (a1),

and also, if desired,

5

(a3) at least one photoinitiator,

(a4) at least one thermal crosslinking initiator,

10

(a5) at least one reactive diluent curable  
thermally and/or with actinic radiation,

(a6) at least one coatings additive, and/or

15

(a7) at least one thermally curable constituent,

with the proviso that the coating material I  
comprises at least one thermally curable  
constituent (a7) if the constituent (a1) contains  
no functional group (a12).

20

11. The clearcoat system A, the multicoat system B,  
the process for producing the clearcoat system A  
or the process for producing a multicoat system B  
as claimed in claim 10, wherein the functional  
groups (a11) and (a21) comprise olefinically  
unsaturated groups or epoxide groups, especially  
olefinically unsaturated groups, hydroxyl groups  
in the case of the functional groups (a12) and
- 25

[lacuna] in the case of the complementary functional groups (a22) and isocyanate groups.

12. The clearcoat system A, the multicoat system B,  
5 the process for producing the clearcoat system A  
or the process for producing a multicoat system B  
as claimed in claim 10 or 11, wherein the  
constituent (a1) comprises a urethane (meth)-  
acrylate and the constituent (a2) comprises a  
10 (meth)acrylate-functional (meth)acrylate copolymer  
containing free isocyanate groups and/or comprises  
a (meth)acrylate-functional polyisocyanate.
13. The use of the clearcoat system A as claimed in  
15 any of claims 1, 2 and 9 to 12, of the multicoat  
systems B as claimed in any of claims 3, 4 and 9  
to 12, of the process for producing the clearcoat  
system A as claimed in any of claims 5, 6 and 9 to  
12, or of the process for producing the multicoat  
20 system B as claimed in any of claims 7 to 12, in  
automotive OEM finishing, automotive refinish, the  
coating of plastics, furniture coating, and  
industrial coating, including coil coating and  
container coating.
- 25
14. A motor vehicle, plastic part, furniture item or  
other part for private or industrial use,  
including a coil or container, comprising at least  
one clearcoat system A as claimed in any of claims

1, 2 and 9 to 12, at least one multicoat system B  
as claimed in any of claims 3, 4 and 9 to 12, at  
least one clearcoat system A produced with the aid  
of the process as claimed in any of claims 5, 6  
5 and 9 to 12, and/or at least one multicoat system  
B produced with the aid of the process as claimed  
in any of claims 7 to 12.




Abstract

Highly scratch-resistant multicoat clearcoat systems and multicoat systems comprising them for primed or  
5 unprimed substrates are producible by

- 10 (1) applying at least one clearcoat film I of a coating material I curable thermally and with actinic radiation to the surface of the substrate, or wet-on-wet to the surface of a basecoat film III, and partially curing it, and
- 15 (2) applying a further clearcoat film II of a coating material II curable with actinic radiation and also, if desired, thermally, comprising nanoparticles, to the surface of the clearcoat film(s) I, and then
- 20 (3) curing the clearcoat films I and II and also, if appropriate, the basecoat film III conjointly with actinic radiation and thermally.

In an alternative embodiment, the clearcoat films I may if desired be cured fully with actinic radiation and  
25 thermally together with the basecoat films III, after which the outer surface of the clearcoats I is roughened, coated with the clearcoat film II, which is cured with actinic radiation and also, if desired, thermally.

 <p><b>DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION</b> (37 CFR 1.63)</p> <p><input type="checkbox"/> Declaration submitted with initial Filing or <input checked="" type="checkbox"/> Declaration Submitted after initial Filing (surcharge) (37 CFR 1.16 (e)) required</p>	<b>Attorney Docket No.</b> IN - 5531 <b>First Named Inventor</b> ALLARD et al. <b>COMPLETE IF KNOWN</b>
	<b>Application Number</b> 10/009,394 <b>Filing Date</b> October 25, 2001 <b>Group Art Unit</b> <b>Examiner Name</b>

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**HIGHLY SCRATCH-RESISTANT MULTI-LAYER PAINT COATING, METHOD FOR PRODUCING THE SAME AND THE USE THEREOF**

(Title of the Invention)

The specification of which:

☐ is attached hereto☒ Was filed on **12. April 2000** as United States Application or PCT International Application Number **PCT/EP00/03267** and was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application

I hereby claim foreign priority benefits under 35, U.S.C § 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate or 365 (a) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate, or any PCT international application(s) having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date DATE/MONTH/YEAR	Priority Not Claimed	Certified Copy Attached?	
				Yes	No
199 20 801.8	GERMANY	6. MAY 1999	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Additional foreign application number are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U.S.C 119(e) of any United States provisional application(s) listed below:

**APPLICATION NUMBER(S)****FILING DATE**

☐ Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto

## DECLARATION — Utility or Design Patent Application

## POWER OF ATTORNEY

☒ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith application and to transact all business in the Patent and Trademark Office connected therewith

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26922

PATENT TRADEMARK OFFICE

or ☐ Correspondence address below

County	United States of America	Telephone	(248) 948-2019	Fax	(248) 948-2093
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name OF SOLE OR FIRST INVENTOR: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle (if any)) Maxime, Euring Augustin Family Name or Surname ALLARD Filip Euring

Inventor's Signature [Signature] Date 27/09/2001

Residence: City	20040 Burago di Molgora, I.T.X.	State	Italy	Country	Italy	Citizenship	French
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DECLARATION —

Utility or Design Patent Application

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☒ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith

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County	United States of America	Telephone	(248) 948-2019	Fax	(248) 948-2093
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name OF SECOND INVENTOR:			<input type="checkbox"/> A petition has been filed for this unsigned inventor		
Given Name (first and middle (if any)) <u>Cyrille</u>			Family Name or Surname <u>JAEQUES</u>		
Inventor's Signature <u>JAEQUES Cyrille</u>			Date		
Residence: City	F-67590	State	France	Country	France
	Schweighouse	FRX		Citizenship	French
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[Page 3 of 4]

Declaration for Utility or Design Patent Application (PTO/SB/01) [1-1.1]

DECLARATION —

Utility or Design Patent Application

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Name of Additional Joint Inventor, If any:

☐ A petition has been filed for this unsigned inventorGiven Name  
(first and middle (if any))

Isabelle

Family Name

KAUFFER

Inventor's

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